Handy's Harbinger

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Problem:

- The accurate computation of ro-vibrational energy levels of polyatomic molecules using potential energy functions
  - H_2O, HCCH, ...

Coordinates are King!

- ▶ Normal modes
  - ▶ KE[1] complicated, BC[2] nasty
- ▶ Polyspherical Orthogonal coordinates
  - ▶ KE and BC simple, PES complicated
- ▶ Bond-Length-Bond-Angle coordinates (Polyspherical Non-orthogonal coordinates)
  - ▶ Quartic PES and BC simple
  - ▶ KE complicated

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[2]Boundary Conditions

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- What is optimum?

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- What is optimum?
    - BLBA: 15.43 cm^{-1} error (1992)
    - Normal from Symmetric Jacobi: 10.79 cm^{-1}
    - Radau: 1.49 cm^{-1}
    - Optimized: 1.29 cm^{-1}

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Chosing coordinates: Step 1

- **X** matrix of nuclear Cartesians $(\vec{X})$
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- Orthogonal coordinates: $\frac{1}{\mu_{\beta\beta'}} = \delta_{\beta\beta'} \frac{1}{\mu_{\beta\beta}}$

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- det $\mathbf{M} \neq 0$, $\beta = N$ c.m. and $\frac{1}{\mu_{N\beta}} = 0$, $\beta \neq N$.

Chosing coordinates: Step 2

- $\mathbf{x} = \mathbf{A}^T(\alpha^{LB}\beta^{LB}\gamma^{LB})\mathbf{x}^{bf}$

- $\mathbf{x}^{bf} = \begin{pmatrix} -r_1\sin(1-a)\chi & r_2\sin a\chi & r_3\sin\theta_3\cos\phi_3 & \dots \\ 0 & 0 & r_3\sin\theta_3\sin\phi_3 & \dots \\ r_1\cos(1-a)\chi & r_2\cos a\chi & r_3\cos\theta_3 & \dots \end{pmatrix}$

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  - basis functions: anything with finite matrix elements

Corrections to Born-Oppenheimer Approximation (2001)

- B.O.: V from $H^{el}\psi^{el} = E\psi^{el}$, $T = -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{m_\alpha}\sum_i \frac{\partial^2}{\partial X_{i\alpha}^2}$

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- 2nd order: ψ^{el} changes, so $V =$same$+C^{(0)}$,
  $T =$same$+\sum_{i\alpha i'\alpha'} C_{i\alpha i'\alpha'}^{(2)} \frac{\partial^2}{\partial X_{i\alpha}\partial X_{i'\alpha'}} + \sum_{i\alpha} C_{i\alpha}^{(1)} \frac{\partial}{\partial X_{i\alpha}}$

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  - $\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}\right)$

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  - $= -\left(\frac{\partial}{\partial r}\right)^\dagger \frac{\partial}{\partial r} - \left(\frac{\partial}{\partial\theta}\right)^\dagger \frac{1}{r^2}\frac{\partial}{\partial\theta} - \left(\frac{\partial}{\partial\phi}\right)^\dagger \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi}$

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- $\frac{\partial}{\partial x_{i\beta}} = \sum_j A_{ji}(\alpha^{LB}\beta^{LB}\gamma^{LB}) \sum_l g_{j\beta l} \hat{O}_l$
  - $\hat{O}_l = \frac{\partial}{\partial r_1}, \frac{\partial}{\partial r_2}, \frac{\partial}{\partial \chi}, ..., \hat{J}_x, \hat{J}_y,$ and $\hat{J}_z$.

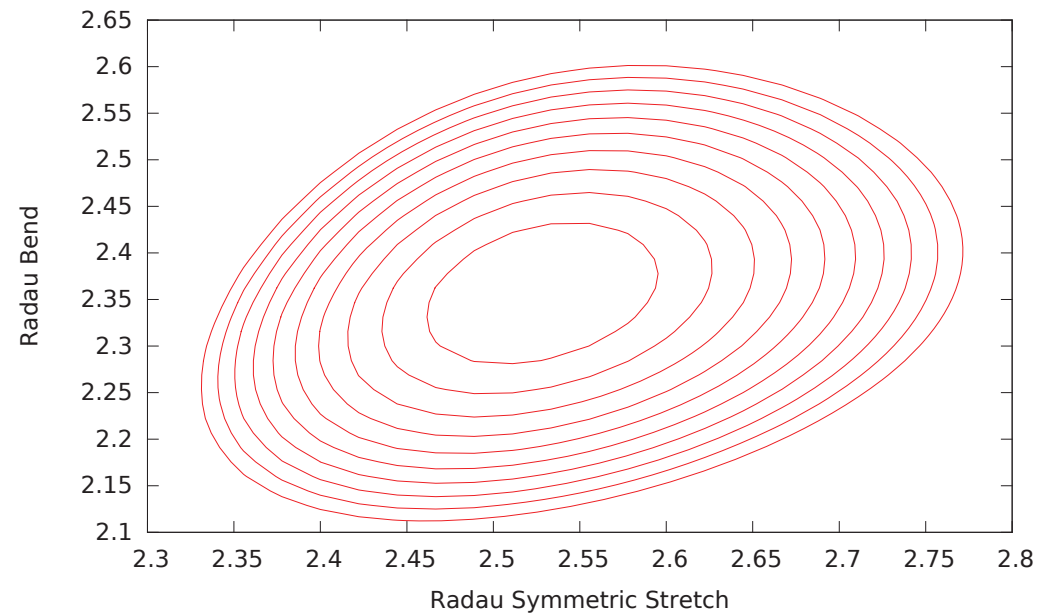# Easier way to derive T

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- for openshell systems ...

What If All Orthogonal Coordinates Not Very Good?

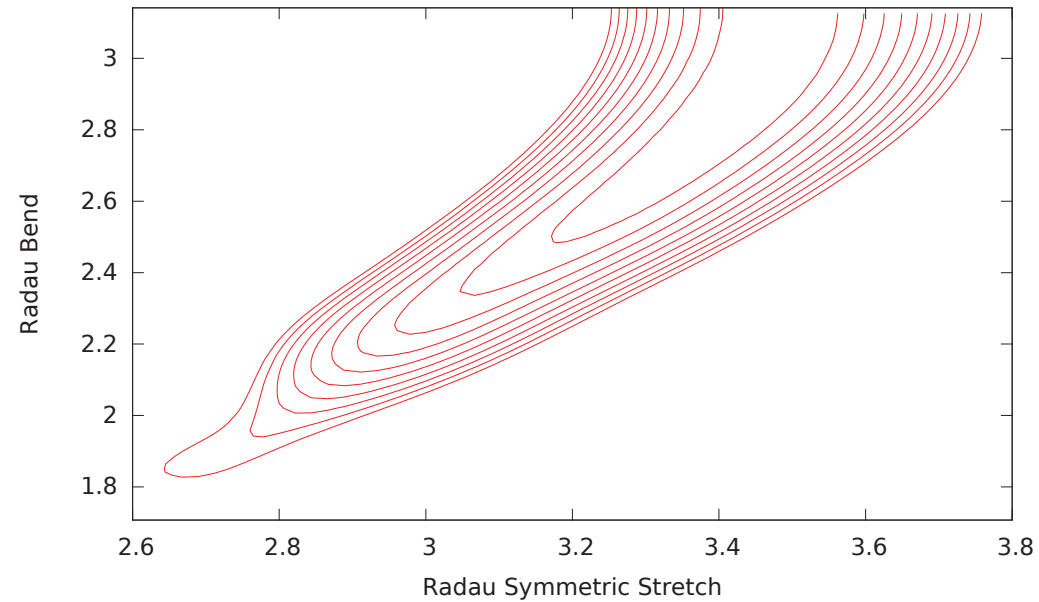# What If All Orthogonal Coordinates Not Very Good?

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- SO$_2$
- C$_3$

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- Repeatedly guess and walk downhill

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- today I embrace generalized coordinates